



Ignition delay, combustion and emission characteristics of diesel engine fueled with biodiesel

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ABSTRACT

Biodiesels are gaining more importance as a promising alternative energy resource. Engine performance and emission characteristics of unmodified biodiesel fueled diesel engines are highly influenced by its ignition and combustion behavior. This review article presents the literature review on ignition delay (ID), combustion and emission characteristics of biodiesel fueled diesel engine. More than hundred articles report which have been published mostly in the last decade are reviewed in this paper. The investigation results report that the combustion characteristics of bio fueled engine is slightly different from the engine running with petroleum diesel. Most of the investigation results have reported that as compared to diesel, biodiesel has early start of combustion (SOC) and shorter ID of between 1–5° and 0.25–1.0°, respectively. Higher cetane number (CN), lower compressibility and fatty acid composition of biodiesel have been identified as the main elements for early SOC and shorter ID. In addition, it is also found that, the heat release rate (HRR) of biodiesel is slightly lower than diesel owing to the lower calorific value, lower volatility, shorter ID and higher viscosity.

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1. Introduction

Diesel engine combustion is a complex phenomenon. Various processes affect the efficient combustion such as, atomization and evaporation of the fuel, mixing of the fuel with surrounding gases, self-ignition, oxidation, turbulence induced by air and fuel jet, the possible interaction of the fuel jet with the cylinder walls, heat

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transfer between the fuel and the surrounding gases, and between combustion gases and the cylinder walls, etc. [1]. The homogeneous air–fuel mixing in time is largely influenced by the combustion chamber geometry and the fuel injection characteristics [2]. Higher the injection pressures the faster the combustion rates resulting higher combustion chamber gas temperature. This is because of the increasing vaporization rate of spray fuel and reduction of its penetration into the combustion chamber [3]. The experimental indicator diagram determines the shape and magnitude of the cylinder pressure diagram. It can also serve the purpose of determining the heat release [4]. The properties of both the pure and blended biodiesel have great influence on the engine performance and emissions, since it has different physical and chemical properties from those of diesel fuel. Further research is required to find out more about the properties of biodiesel and their effects on the combustion and the fuel injection system, if this fuel is used in the diesel engines without any modification [5]. Though several advantages can be obtained with the application of biodiesel, few of its inherent properties are to be ameliorated in order to overcome the limitations [6]. Biodiesel has higher viscosity than petroleum diesel [7]. Studies have shown that increasing blend ratios and thus viscosity, can lead to reduced atomization quality of the injected fuel. The consequences are increasing in the average droplet diameter of the sprayed fuel and the breakup time [8–11]. The injected fuel quantity, injection timing, and spray pattern can be affected by the higher viscosity and specific gravity of the biodiesel. Combustion and HRR characteristics of biodiesel must be known in order to achieve the reduction of brake specific fuel consumption (BSFC) and emission while keeping other engine performance parameters at an acceptable level. The differences in physical properties between diesel and biodiesel fuels affect the combustion and heat release characteristics [5,8,12–15]. Numerous studies have been conducted on ID and combustion behavior of diesel engine fueled with biodiesel. The different varying parameters of these studies were different, fuel injection timing, injection pressure, engine load, compression ratio etc. Results of the studies revealed that biodiesel has early SOC, shorter ID and lower HRR. Biodiesel has lower calorific value thereby causes specific power loss [14,16,17]. The tests conducted at steady state conditions in a four-cylinder turbocharged DI diesel engine at full load and 1400-rpm engine speed. The results showed that pure biodiesel (B100) had 13.8% higher BSFC as compared to diesel. This is mainly because of lower heating value of biodiesel of 39871 kJ/kg as compared to diesel of 45339 kJ/kg. Therefore biodiesel contains about 12% less heating value than diesel [14]. However, the addition of selective additives in the biodiesel ameliorates this shortcoming of specific power output. Several techniques such as

application of a turbocharger in the diesel engine, viscosity reduction additives, preheating, exhaust gas recirculation (EGR), doping, per-oxidation technique, and low heat rejection (LHR) concept, etc. have been employed in the large scale application of biodiesel.

Most of the studies have reported that the combustion behavior of biodiesel and diesel are not identical. Even though biodiesel possesses many advantages over diesel fuel however, some properties including viscosity, volatility and compressibility of the biodiesel which affects the ID and combustion behavior are needed to be improved. This review describes a brief overview of the work done so far regarding ignition delay, combustion and emission characteristics using biodiesel. The data presented in this article from the authentic sources would guide the researchers in future to select their appropriate pathway.

2. Combustion background in diesel engine

Diesel engines operate on the principle of compression ignition. Therefore, these engines rely on compression in the cylinder to raise the air temperature and pressure such that upon injecting fuel, the air–fuel mixture auto ignites. The injected fuel spray needs to be finely scattered to evaporate and mix readily. This mixture should mix with the rapidly swirling hot air in the combustion chamber. Generally, high compression ratios in the order of 12–24 are used in diesel engines to ensure high temperature and pressure, and thus auto ignition of the fuel–air mixture. Therefore, the combustion process in compression ignition engines can be divided into three major sections, as shown in Fig. 1 [18].

2.1. Ignition delay

As shown in Fig. 1, ID represented by AB has been considered very important parameter in combustion phenomenon [8]. This period is also called the preparatory phase during which some fuel has already been admitted into the combustion chamber, but ignition has not yet commenced. This period is counted from the start of fuel injection into the combustion chamber to the point where the pressure–time curve separates from the motoring curve indicated as SOC. Delay period in the diesel engine exerts a very great influence on both engine design and performance. The delay period has been found to be different when diesel and biodiesel are used individually. Their effects are discussed elaborately in Section 3. Functionally, the ID can be divided into two parts, such as the physical delay and chemical delay as shown in Fig. 2 [19].

2.1.1. Physical delay

It is the time between the beginning of injection and the attainment of chemical reaction conditions. During this period, the fuel is atomized, vaporized, mixed with air and raised to self-

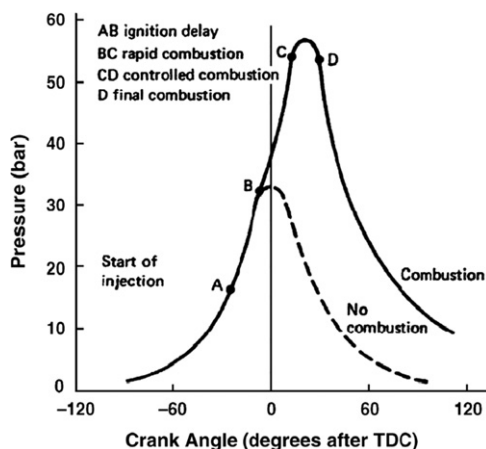


Fig. 1. Different stages of combustion in CI engines [18].

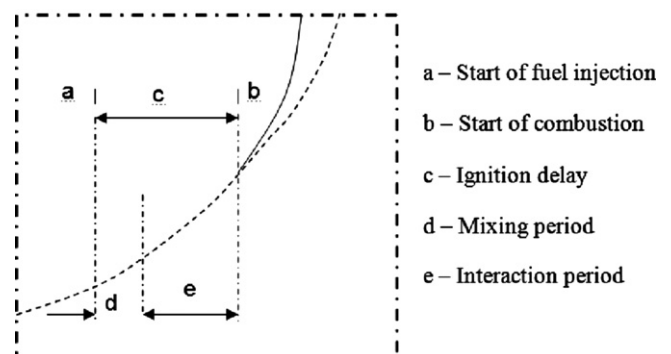


Fig. 2. Extended view of ignition delay [19].

Table 1
Effect of different biodiesels on ignition delay and injection timing in comparison to diesel.

Ref. no.	Authors	Biodiesel feedstock	CN of biodiesel as compared to diesel	Engine type	Remarks
[5]	Qi et al.	Soybean crude oil	Higher	Single cylinder, 4-stroke, DI diesel engine.	Shorter ignition delay and earlier start of combustion
[14]	Canakci	Soybean oil	Slightly higher	Turbocharged DI diesel engine	Shorter ignition delay
[23]	Senatore et al.	Rapeseed oil methyl ester (ROME)	Higher	Turbocharged DI diesel engine	Early start of injection
[24]	Canakci and Van Gerpen	Soybean oil and yellow grease with 9% free fatty acids	Higher	Direct injection (DI) diesel engine	Shorter ignition delay and early start of injection timing
[26]	Rao et al.	Used Cooking oil Methyl Ester (UCME) and its blends	Higher	Direct injection C.I. engine.	Shorter ignition delay (ID) which decreases with the increment of % UCME in the blend
[29]	Ozsezen et al.	waste (frying) palm oil methyl ester (WPOME) and canola oil methyl ester (COME)	Higher	DI diesel engine	Slightly shorter ignition delay

ignition temperature. Viscosity governs the physical delay of fuel combustion process, for low viscosity fuels, the physical delay is small and vice versa.

2.1.2. Chemical delay

During this period reactions start slowly and then accelerate until inflammation or ignition takes place. Generally, chemical delay is larger than the physical delay. However, it depends on the temperature of the surroundings. Chemical reactions are faster at higher temperatures thus physical delay becomes longer than the chemical delay.

2.2. Rapid or uncontrolled combustion

In this phase, some of the mixture that has been injected into the cylinder during the ID phase, auto-ignites and starts to combust as a premixed charge. A rapid rise in pressure takes place. The rate and extent of the pressure increase depend on the amount of fuel presents in the combustion chamber which in turn depends on the length of the ID [18,20].

2.3. Controlled combustion

Continual rate of injected fuel mixing with the hot compressed air in the cylinder mainly controls the combustion behavior. As the piston backs away, expansion rapidly cools the in-cylinder mixture resulting in a dramatic decrease in chemical reaction rates. The rate become so low that the term “frozen” is often applied, meaning the reaction rates are insignificant, leaving the system in a state that may be far from chemical equilibrium. High level of NO_x is the example of chemical product that is “frozen” well above their equilibrium level [18].

3. Ignition delay of biodiesels

Changes in both the injection timing and SOC affect ID. Whereas, the change in fuel properties influences it. The lower compressibility and the viscosity of the biodiesel lead to an advanced start of injection [21]. The start of fuel injection is usually taken as the time when the injector needle lifts off its seat, and the SOC can be defined by the change in slope of the heat-release rate that occurs at ignition. The start of fuel injection is an important feature as it affects the combustion characteristics, exhaust gas temperature and exhaust emissions of the engine. Ignition delay is governed by the CN. Effect of different biodiesels on ID and injection timing in comparison to diesel is presented in Table 1. The lower compressibility and density of the biodiesel

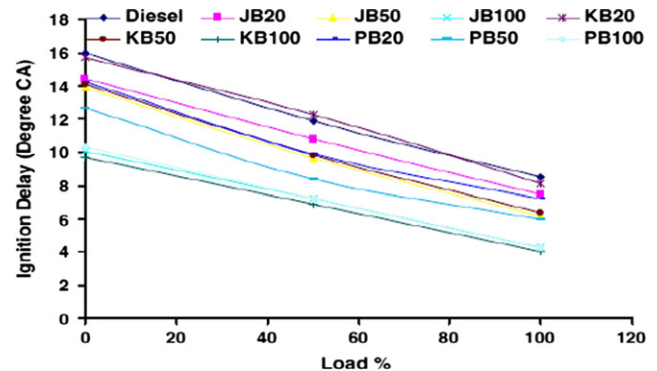


Fig. 3. Effect of load on the ignition delay for diesel, biodiesel and their blends [32].

cause the shorter ID or earlier injection timing that results in, advanced combustion as well. Usually, the early injection leads to higher combustion temperatures, although the premixed combustion period is reduced due to the shorter ID [22]. Senatore et al. [23] reported the earlier start of fuel injection using the rapeseed oil methyl ester (ROME) as compared to diesel. Experimental study conducted by Canakci and Van Gerpen [24] in John Deere 4276 T model diesel engine using soybean oil methyl ester (SOME) and yellow grease methyl ester (YGME). Results implied that the SOC for SOME and YGME are 3.4° and 4.2° earlier than that of diesel fuel. In addition, the shorter ID of 0.75° and 0.63° for SOME and YGME were found as compared to diesel. The early SOC and shorter ID is attributed the fact of higher cetane number of SOME of 51.5 and YGME of 62.5 as compared to diesel of 42.6. Likewise, Monyem [25] obtained the shorter ID of 0.6° using SOME as compared to diesel fuel. The effect of engine load on ID for four-stroke constant speed direct injection (DI) diesel engine using used cooking oil methyl ester (UCME) is presented by Rao et al. [26]. According to the results, the ID of UCME is significantly lower than diesel and decrease with increasing percentage of UCME in the blend. At maximum load of 4.4 kW, the ID of 15° crank angle (CA) was obtained for diesel and this is followed by 14.1° CA for 20% UCME, 13.8° CA for 40% UCME, 13° CA for 60% UCME, 12.7° CA for 80% UCME and 12.6° CA for 100% UCME. They explained that this is because of the oleic and linoleic fatty acid methyl esters present in the UCME split into smaller compounds when it enters the combustion chamber resulting in higher spray angles and hence causes earlier ignition. They also found that the reduction in the ID increase with increasing load. This may be attributed to the higher combustion temperature and exhaust gas dilution at higher load. Another study was conducted by Ozsezen

and Canakci [27] using waste palm oil methyl ester (WPOME) and canola oil methyl ester (COME). This study reports the earlier SOC for biodiesels as compared to diesel. The average SOC timing of the WPOME and COME was occurring at 9.35° CA before top dead center (BTDC) and 8.55° CA BTDC, respectively, while the SOC timing in the case of diesel was taken place at 8.15° CA BTDC. Therefore, the use of the WPOME and COME, the average earlier SOC are 1.2° CA and 0.4° CA, respectively as compared to diesel.

Nwafor et al. [28] reported that biodiesel having a slightly lower CN may exhibits longer delay periods as well as slower burning rate, hence resulting in delay of combustion, higher exhaust and lubricating oil temperatures. Comparative study on combustion characteristics of diesel and biodiesel from soybean oil was conducted by Canakci et al. [14]. The test was performed at steady state conditions in a four-cylinder turbocharged DI diesel engine at 1400 rpm. The CNs for diesel and biodiesel was 42.6 and 51.5, respectively. The biodiesel showed the shorter ID of about 1.06° diesel fuel. Another study conducted on a DI diesel engine fueled with biodiesels from WPOME and COME at constant engine speed of 1500 rpm under the full load condition. The ID for WPOME, COME and the petroleum diesel was found at 7.50° CA, 8.0° CA and 8.25° CA, respectively [29]. Likewise, shorter ID of SOME as compared to diesel was reported by Zhang and Gerpen [30] and McDonald et al. [31]. To investigate the effect of engine load on ID was conducted by Sahoo and Das [32] in a single cylinder diesel engine, using diesel and biodiesel from jatropha, karanja and polanga. Results showed that the ID of biodiesel and their blends were found to be shorter than that of diesel. The results are presented in Fig. 3. Ignition timing is delayed proportionally with the increase of the biodiesel in the blends. The duration of combustion is shorten for all biodiesel blends while the

brake thermal efficiency (BTE) increases from medium to full load condition, which can be attributed to the oxygen content increases in the blends [33]. Biodiesel usually includes a small percentage of diglycerides having higher boiling points than diesel. However, the chemical reactions during the injection of biodiesel at high temperature resulted in the breakdown of the high-molecular weighted esters. These complex chemical reactions led to the formation of gases of low-molecular weight. Rapid gasification of this lighter oil in the fringe of the spray spreads out the jet, and thus volatile combustion compounds ignited earlier and reduced the delay period. Biodiesel derived from jatropha, karanja and polanga oil having higher molecular weight is likely to react identically. Rodriguez et al. [34] conducted an experiment using biodiesel derived from palm and rapeseed biodiesel and diesel and found that biodiesel has the shorter ID as compared to diesel. This observation resembles with the results of other researchers as well [35,36]. The shorter ID of biodiesel is also due to the presence of rich oxygen content in the biodiesel [37,38].

4. Combustion characteristics of biodiesel

In this section, the review of combustion characteristics in terms of in-cylinder pressure, the rate of pressure rise, and HRR of biodiesel fuel used in the diesel engine has been presented with some brief discussion. The maximum HRR of 71.459 J/°. CA has been recorded for diesel at 6° BTDC while the maximum HRR of 51.481 J/° is recorded for UCME at 8° BTDC [26]. Study conducted by Ozsezen et al. [29] was carried out in water-cooled, DI, naturally aspirated and four stroke six cylinder 6.0L Ford Cargo

Table 2
Combustion characteristics of the biodiesel for different engine conditions [8].

			10 Nm					20 Nm				
			B0	B5	B20	B50	B100	B0	B5	B20	B50	B100
Original Injection timing (20 °CA BTDC) Compression ratio (18) Injection pressure (20 MPa)	Maximum CGP (MPa)	Maximum CGP (°CA ATDC)	7.05	7.02	6.97	6.82	6.61	7.96	7.94	7.9	7.71	7.54
	Maximum ROPR (MPa/deg)	Start of combustion (°CA BTDC)	4.52	4.85	5.18	4.97	5.84	3.2	2.87	3.76	3.86	4.52
	Ignition delay (°CA)		0.39	0.39	0.38	0.37	0.37	0.5	0.49	0.49	0.46	0.46
			5.97	6.11	6.63	6.44	7.29	9.27	9.6	9.93	10.07	10.92
			14.3	13.9	13.37	13.57	12.71	10.73	10.4	10.07	9.94	9.08
Injection timing (15 °CA BTDC)	Maximum CGP (MPa)	Maximum CGP (°CA ATDC)	6.56	6.56	6.48	6.34	6.1	7.15	7.14	6.99	6.85	6.64
	Maximum ROPR (MPa/deg)	Start of combustion (°CA BTDC)	6.17	6.5	6.83	7.16	7.82	4.19	4.52	5.18	5.51	5.84
	Ignition delay (°CA)		0.35	0.35	0.34	0.32	0.29	0.45	0.44	0.43	0.42	0.38
			2.67	2.73	2.48	3	3.47	5.97	6.25	6.57	6.63	6.77
			12.33	12.53	12.12	12	11.54	9.03	8.56	8.37	8.32	8.24
Injection timing (25 °CA BTDC)	Maximum CGP (MPa)	Maximum CGP (°CA ATDC)	7.36	7.32	7.24	7.13	7.06	8.5	8.47	8.42	8.34	8.21
	Maximum ROPR (MPa/deg)	Start of combustion (°CA BTDC)	2.54	2.87	2.87	3.2	3.53	2.21	1.13	1.12	1.54	1.55
	Ignition delay (°CA)		0.45	0.45	0.45	0.44	0.43	0.6	0.59	0.58	0.56	0.54
			8.75	8.74	16.06	8.61	8.94	12.05	13.13	13.23	13.04	13.89
			16.2	16.21		16.39	16.06	12.96	11.77	11.56	11.97	11.11
Compression ratio (20)	Maximum CGP (MPa)	Maximum CGP (°CA ATDC)	7.9	7.87	7.8	7.64	7.5	8.95	8.93	8.84	8.65	8.48
	Maximum ROPR (MPa/deg)	Start of combustion (°CA BTDC)	3.54	3.53	3.59	3.86	3.86	1.8	1.55	1.88	2.21	3.2
	Ignition delay (°CA)		0.53	0.55	0.51	0.48	0.46	0.71	0.67	0.65	0.61	0.57
			5.78	5.86	6.63	6.44	6.77	9.6	9.42	9.41	9.41	9.74
			13.23	13.11	12.37	12.57	12.24	9.4	9.58	9.6	9.59	8.87
Injection pressure (24 MPa)	Maximum CGP (MPa)	Maximum CGP (°CA ATDC)	7.04	7.01	6.98	6.92	6.87	7.94	7.94	7.88	7.79	7.66
	Maximum ROPR (MPa/deg)	Start of combustion (°CA BTDC)	4.19	4.23	4.52	4.68	5.18	2.54	2.87	3.2	4.19	4.85
	Ignition delay (°CA)		0.44	0.43	0.42	0.39	0.36	0.55	0.54	0.52	0.5	0.45
			7.19	7.2	7.29	7.32	7.62	10.47	10.53	10.59	10.67	11.25
			12.94	12.83	12.71	12.56	12.38	9.48	9.41	9.38	9.31	8.75

diesel engine using COME and WPOME. Investigation result reported that maximum HRR of $0.41 \text{ kJ}/^\circ \text{CA}$ was obtained at 5.6° BTDC for diesel while, maximum HRR of $0.73 \text{ kJ}/^\circ \text{CA}$ at 4.5 BTDC was found for COME and maximum HRR of $0.34 \text{ kJ}/^\circ \text{CA}$ at 5.8° BTDC was obtained for WPOME. On the other hand Canakci [14] showed the HRR of $0.12 \text{ kJ}/^\circ$ at 4.8 CA for diesel while for biodiesel from soybean oil, the HRR of $0.10 \text{ kJ}/^\circ \text{CA}$ was recorded at 7.5 CA . On the other hand some authors [39,40] reported that, along with shorter ID, biodiesel offers higher ignition temperature, cylinder pressure and peak HRR. In this regard, similar results have been reported by Ozsezen et al. [29] using biodiesel from WPOME and COME. The peak cylinder gas pressure for WPOME and COME were measured by 8.34 MPa and 8.33 MPa , respectively at 6.75° CA after top dead center (ATDC), while the peak cylinder gas pressure for diesel was 7.89 MPa at 7° CA ATDC . Due to biodiesels' higher BSFC, CN, boiling point, oxygen content, and advance in the start of injection (SOI) timing, the maximum cylinder gas pressures of the biodiesels were higher than that of the petroleum diesel. The recent investigation carried by Gumus [8] in Lombardini 6LD400 single cylinder diesel engine using Hazelnut kernel oil methyl ester with various condition which has been presented in Table 2. Combustion characteristics of a single cylinder, 4.4 kW DI compression ignition engine coupled with swinging field electrical dynamometer fueled with used cooking oil methyl ester (UCME) and its blends were analyzed, and compared to the baseline diesel fuel [26]. The combustion performance was measured using AVL indimeter software which was interfaced with the engine. The experimental results showed that peak cylinder pressure for UCME and its blend was $2.2\text{--}4.4\%$ higher as compared to that of diesel. The maximum HRR due to UCME combustion has been observed as $51.481 \text{ J}/^\circ \text{CA}$ at 8° BTDC while, the HRR for diesel has been recorded as $71.459 \text{ J}/^\circ \text{CA}$ at 6° BTDC [26]. The lower HRR of UCME as compared to diesel is due to the shorter ID and longer combustion duration. The total heat release was decreased by using biodiesel derived from rice oil. The lower heating value of biodiesel increased the specific fuel consumption by 5.9% as compared to petroleum diesel fuel. In addition, by increasing the biodiesel concentration in the blend, the total amount of heat release at premixed combustion was reduced due to shorter ID [41]. Another study was presented by Sahoo and Das [32] at various load using diesel and biodiesel from polanga, jatropha and karanja. Results reported that at peak load, polanga biodiesel (PB100) had 8.5% higher peak pressure than that of neat diesel and this was followed by jatropha biodiesel (JB100) of 7.6% and karanja biodiesel (KB100) of 6.9% . A similar trend was observed while the engine was operated at half load and no load conditions. The maximum HRR of all biodiesels and

their blends was lower than that of diesel. This is because of the shorter ID and lower premix combustion phase for biodiesel and their blends. On the other hand, while running with a diesel, increased accumulation of fuel during the relatively longer delay period resulted in higher rate of heat release. Engine cylinder pressure and net HRR were analyzed by Tsolakis et al. [42] using different blends of ROME and diesel at engine operating condition of 4.5 bar indicated mean effective pressure (IMEP) and 6.1 bar IMEP. According to their analysis, it was found that with the increasing RME percentage in the fuel blends, the ID tends to reduce and the rate of fuel burnt in the pre-mixed phase increased. At an operating condition of 4.5 bar IMEP , the overall combustion durations were 30° CA , 30° CA , 28° CA and 28° CA for B0 (diesel), B20, B50 and B100 (pure biodiesel), respectively while, at the operation condition of 6.1 bars IMEP , the combustion duration was 34° CA for all the fuel. The combination of the increased injection pressure and similar CN of RME compared to diesel resulted in an increased amount of fuel undergoing premixed combustion at an earlier stage as indicated by the net HRR trends shown in Fig. 4a and b.

A study [8] was conducted by using hazelnut kernel oil methyl ester and its blends, and results implied that peak cylinder gas pressure (PCGP) was found to be increasing for the engine load (EL) of 10 N m due to increased biodiesel blend ratio. The PCGP occurred between 6.61 MPa and 7.05 MPa at the EL of 10 N m while the PCGP was obtained between 7.54 MPa and 7.96 MPa for the EL of 20 N m . A study conducted using COME and WPOME and compared with petroleum diesel, the result reported that due to shorter ID and advanced injection, the combustion started advance by 1.2° CA and 0.4° CA for WPOME and COME, respectively. Both the biodiesels (WPOME and COME) had taken the prolonged time for pre-mixed combustion. Shorter ID and advanced injection influence the combustion starting time, duration, and peak cylinder pressure. The investigation results with regards to the HRR for both the diesel and the biodiesel from waste oil revealed that the overall HRR during combustion is lower for the B50 fuel compared to petrodiesel. The maximum HRR of $1.27 \text{ kJ}/\text{cycle}$ and $1.6 \text{ kJ}/\text{cycle}$ were found for B50 and diesel, respectively. The lower HRR of biodiesel is due to the lower heating value of waste oil biodiesel [43].

5. Effect of biodiesel characteristic on combustion performance

The specific energy content of biodiesels is lower than diesel. Biodiesels have about 9% lower heating value as compared to diesel, consequently the BSFC increases with increasing biodiesel

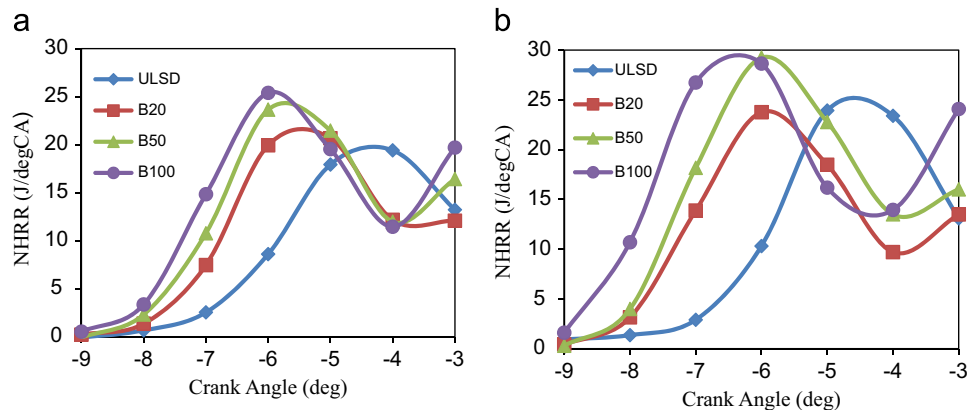


Fig. 4. (a) Pre-mixed combustion NHRR trends with different fuel blend at IMEP 4.5 bar [42]. (b) Pre-mixed combustion NHRR trends with different fuel blends at IMEP 6.1 bar [42].

Table 3

Structural formula and fatty acid composition of different biodiesel fuel [60–65].

FAME Composition (wt%)	C:N	Chemical structure	Elementary formula	Biodiesel feedstock							
				Coconut	Jatropha	Palm	Soybean	Sunflower	Peanut	Tallow	Canola
Lauric	C12:0	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	$\text{C}_{12}\text{H}_{24}\text{O}_2$	45.6	0.0	0.2	–	–	–	0.1	–
Myristic	C14:0	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	$\text{C}_{14}\text{H}_{28}\text{O}_2$	22.1	0.1	0.8	0.1	0.1	–	3.3	0.1
Palmitic	C16:0	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	$\text{C}_{16}\text{H}_{32}\text{O}_2$	10.2	15.6	39.5	10.3	6.0	10.4	25.2	3.9
Stearic	C18:0	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	$\text{C}_{18}\text{H}_{36}\text{O}_2$	3.6	10.5	5.1	4.7	5.9	8.5	19.2	3.1
Oleic	C18:1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$\text{C}_{18}\text{H}_{34}\text{O}_2$	8.2	42.1	43.1	22.3	20.43	47.1	48.9	60.2
Linoleic	C18:2	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$\text{C}_{18}\text{H}_{32}\text{O}_2$	2.7	30.9	10.4	54.1	66.2	32.9	2.7	21.1
Linolenic	C18:3	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$\text{C}_{18}\text{H}_{30}\text{O}_2$	0.0	0.2	0.1	8.3	0.6	0.5	0.5	11.1
Others				7.6	0.6	0.8	0.2	–	0.6	0.1	0.5
Saturated fatty acids (%)				81.5	26.2	45.6	37.4	32.43	66	96.7	67.3
Unsaturated fatty acids (%)				10.9	73.2	53.6	62.6	67.57	34	3.3	32.7

Where, C:N, C the number of carbons and N the number of double bonds of carbons in the fatty acid chain.

ratio in the blends [21,44–47]. Biodiesel blends are usually formed, mixing with ordinary diesel at a different mixing ratio. From the several studies, it has been observed that mixing of blends is crucial for combustion and emission characteristics. An investigation carried by Lee et al. [9] was to observe the combustion and emission characteristics of the biodiesel fueled common rail injection diesel engine with various mixing ratios. The result implied that due to higher viscosity and surface tension, the size of the droplet increased with an increasing mixing ratio of the biodiesel. However, the emission parameters were decreasing with increasing biodiesel blend ratios though the NO_x was increased slightly due to shorter ID. The physical properties, like kinematic viscosity, cetane number and surface tension, of biodiesels are different from the petroleum diesel. Both the kinematic viscosity and the surface tension are co-related to combustion and atomization behavior. These two properties of the biodiesel increase with increasing percentage of blends in the fuel. Since the biodiesels possess higher cetane number which leads to the advanced ignition and consequently, higher NO_x formation [9]. A study conducted by Sahoo and Das [48] with non-edible jatropha, karanja and polanga biodiesel in different blends percentage in a single cylinder, 4-stroke diesel engine and the result implied that polanga biodiesel has the highest cylinder peak pressure, which is followed by jatropha and karanja for entire load conditions. It was also noticed that higher cylinder pressure is observed in accordance with the blends concentration [48]. Qi et al. [49] conducted an experiment to investigate the combustion and emission performance using biodiesel and ethanol biodiesel micro-emulsions and reported that micro-emulsion delays the SOC compared to biodiesel and improve the combustion characteristics. However, the micro-emulsion increases the HC, CO emission as well as specific fuel consumption. A study was carried out with diesel fuel and different percentages like 5%, 10%, and 15% by vol. of ethanol blended biodiesel and the results revealed that the maximum pressure and heat release were increased with blend percentage as compared to diesel. The 5% ethanol blend increased the thermal efficiency slightly while there were no significant differences with 10% and 15% blends as compared to diesel. Ethanol blended biodiesel decreases the NO_x emission and smoke opacity of 35–85% [50]. Similar result was also obtained by Lu et al. [51]. A comparative study conducted by using a combination of biogas–biodiesel as a dual fuel and biodiesel from soybean oil methyl ester as a single fuel to investigate the combustion and emission performance [52]. It was found that, the increasing rate of biogas in dual fuel leads to decrease the combustion pressure and HRR. As compared to single fuel, the dual fuel increased the ID and combustion duration while the indicated mean effective pressure was decreased slightly [52]. On the other hand, Yoon and Lee [53]

stated that dual fuel increases the peak cylinder pressure, rate of heat release and IMEP slightly, as compared to diesel and biodiesel. Properties of different types of biodiesel fuels have a strong relation with their fatty acid composition. Because the structure of the fatty compounds in fuel can also affect many properties such as, cetane number, viscosity, density, heating value and low temperature properties etc. Thus the fuel properties can influence the fuel droplet size and size distribution, spray characteristics, fuel evaporation, flame propagation and species temperature [54,55]. Generally, cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation of the FAME molecule. In addition, the heating value, melting point, cetane number, viscosity and oxidation stability decreases whereas density, bulk modulus, fuel lubricity and iodine value increases as the degree of unsaturation increases. It has also been observed that, the biodiesel molecular structure has a substantial impact on combustion and hence emissions [56–59]. Moreover, structural formula and fatty acid composition of some biodiesel fuels can be found in Table 3.

6. Different techniques and strategies to improve the combustion performance of biodiesel

Despite of many advantages of biodiesel, several properties that need to be further improved. After transesterification, its viscosity and density remain higher than that of diesel fuel. It is well known that the viscosity of fuels affects some processes such as atomization, vaporization, fuel–air mixing and so on. According to Lefebvre [66], atomization in a diesel engine is affected by the physical properties such as: viscosity, density, and surface tension of a liquid fuel. The higher viscosity and density of biodiesel from ROME were compensated with the application of the turbocharger in a diesel engine [67]. The turbine of the turbocharger is driven by the energy available in the exhaust gas and the compressor, which is coupled to turbine with a shaft, ensures higher temperature and pressure as well as more air into the cylinder at the timing of the injection. Thus, it provides better combustion and improves brake power. Consequently the BTE increases with a trade-off of increasing of NO_x than that of diesel fuel. In order to reduce the viscosity, two approaches were used: (i) heating the Jojoba Methyl Ester (JME) fuel to different temperatures just before entering the fuel-injection pump and (ii) by adding viscosity reduction additive (Diethyl Ether) to the JME [68]. The viscosity was reduced by both approaches. According to the investigation [68], the effects of adding additive to JME decreased the ignition delay period of 2–7° depending on the load. This may be attributed to the higher amount of fuel injected

thereby, higher cycle temperatures that reduced the ignition delay period. Similarly, the effect of heating the JME to 50 °C and 70 °C as compared to JME at room temperature reduced the ignition delay period of 5–15°. The peroxidation technique can be applied to reduce compounds of high molecular weight and viscosity [69]. In the peroxidation process, either hydrogen peroxide or an ozone compound can be used. Low heat rejection (LHR) engine (the engine with thermal barrier coating is called LHR engine) can also provide improved fuel economy, reduced engine noise, higher energy in the exhaust gases and multi fuel capability of operating low cetane fuels. The LHR concept is based on suppressing heat rejection to the coolant and recovering the energy in the form of useful work. The increased in-cylinder gas and cylinder liner temperatures of the LHR engine make possible the usage of biodiesel without preheating [70]. Therefore the energy of biodiesel can be released more efficiently. Combustion characteristics of low heat rejection (LHR) diesel engines have reported in four ways by Sun et al. [71] when compared to standard diesel engines: (i) ID period shortens, (ii) diffusion burning period increases while premixed burning period decreases, (iii) total combustion duration increases and (iv) heat release rate in the diffusion burning period decreases. A test conducted by Karabektas et al. [72] in a single cylinder four-stroke DI diesel engine using cottonseed oil methyl ester (CSOME). Before entering into the combustion chamber biodiesel was heated to different temperatures of 30 °C, 60 °C, 90 °C and 120 °C to investigate the effect of preheating on BTE along with CO and NO_x emissions. The results showed that preheating the biodiesel up to 90 °C leads to positive effect on the BTE and CO emission, but negative effect on NO_x emission. Preheating the biodiesel to 120 °C tend to reduce the brake power due to excessive fuel leakage owing to lower fuel viscosity.

7. Effect of biodiesel on emission behavior

As biodiesel is an oxygenated fuel, which undergoes improved combustion in the engine due to the presence of molecular oxygen, which also leads to higher NO_x emissions. Not only that injection timing, premixed combustion and fuel chemistry are also responsible for higher NO_x [73]. Dorado et al. [74] tested in a three-cylinder, four-stroke DI diesel engine using olive oil methyl ester and diesel and found stable combustion efficiency for both fuels. The exhaust emissions were reduced significantly, which are 58.9%, 32%, and 8.9% in the case of CO, NO_x, and CO₂, respectively as compared to diesel. In addition, a slight reduction of BSFC was also found when olive oil methyl ester is used. Biodiesel contains 11% oxygen content which leads to burn the fuel completely during combustion thereby the formation of HC emission become lower [75]. A study conducted by Canakci [14] using soybean oil biodiesel and petroleum diesel fuel in a turbocharged DI diesel engine at engine speed of 1400 rpm to observe the emissions and BSFC behaviors. The results showed that biodiesel offer higher BSFC and NO_x emission. Controlling of the NO_x emissions primarily requires the reduction of in-cylinder temperatures. Therefore, this higher NO_x emission can be controlled by employing EGR system [42,76–85]. Zheng et al. [44] adopted the EGR system to investigate the low temperature combustion in a single cylinder DI diesel engine with various biodiesels and diesel. The biodiesel fuels were soy, canola and yellow grease and diesel was ultralow sulfur type. The observations reported the simultaneous NO_x and soot reduction when the ID was more than 50% with 0% EGR. In addition, lowest NO_x emission was found using 55% and 65% EGR for the engine operating condition of 4.4 bar BMEP and 3.1 bar BMEP, respectively. Recycled exhaust gas lowers the oxygen concentration in

the combustion chamber and increases the specific heat of intake charge which results in lower flame temperature. Reduced oxygen and flame temperature leads to lower NO_x formation. However, application of EGR also resulted in some penalties [76]. Soot is the primary means of radiation heat loss from an in-cylinder flame and biodiesel produces less soot because it is an oxygenated fuel. Therefore, radiative heat losses are lower for biodiesel flames, which produce higher flame temperature and more NO_x [15,86].

8. Effect of additives on performance and emission

The use of additives on the performance of diesel engine have already been studied by several researchers and found promising results. But the types of additives which would be used in the engine should be selective. Keskin et al. [87] reported that Mg and Mo based additives mixed with tall oil biodiesel did not work properly to improve the performance of the engine. One of the limitations of biodiesel is its flow properties at the low temperatures caused by higher density and viscosity. An investigation was carried out to improve the cold flow properties, combustion and emission performance of biodiesel fueled engine by infusing several additives like ethanol, methanol, kerosene and orange oil, and found favorable results. Especially ethanol additives showed the significant results to enhance the combustion and emission performance [88]. Effective additives are imperative to improve the fuel properties of biodiesel fuels to obtain the effective engine performance and controlled NO_x emission [89,90]. Emission characteristics of biodiesel and its blends as compared to petroleum diesel are presented in Table 4 [91].

Investigations have been carried out to reduce the NO_x emission from the biodiesel and in this respect, the use of antioxidants/additives with biodiesel can be effective to control the NO_x [92,93]. Recently, Varatharajan and Cheralathan [94] and Varatharajan et al. [95] studied the effect of antioxidants on the emission behavior of the soybean biodiesel and jatropha biodiesel, respectively. Study result found the significant reduction of NO_x emission by the addition of antioxidants but smoke, CO and HC emissions were found to have increased. The National Renewable Energy Laboratory's (NREL) report named "NO_x Solutions for

Table 4

Average mass emissions changes using the biodiesel mixtures relative to the standard diesel fuel (%) [91].

Mixture	Co	NO _x	So ₂	Particular matter	Volatile organic compounds
B20	−13.1	+2.4	−20	−8.9	−17.9
B100	−42.7	+13.2	−100	−55.3	−63.2

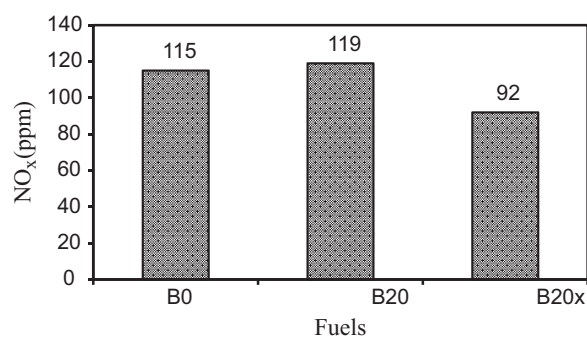


Fig. 5. NO_x emission at constant load of 50 N m and engine speed of 2250 rpm [100].

Biodiesel” reported that di-tertiary butyl peroxide and ethylhexyl nitrate, which are both cetane improvers effectively reduce the NO_x emission. NREL also reports that tertiary butylhydroquinone, an antioxidant, is an effective NO_x -reducing agent, with slight PM increase [96]. Hess et al. [97], carried out a study in a single cylinder, direct-injection, air-cooled, naturally aspirated Yanmar engine using 20% soy biodiesel with and without antioxidant (butylated hydroxyanisole or butylated hydroxytoluene). The result also illustrated that NO_x emission was reduced significantly with the addition of antioxidant. Keskin et al. [98] examined the effectiveness of metallic based fuel additive in tall oil methyl ester and diesel fuel. The test was carried out in an unmodified DI diesel engine and result revealed significantly lower NO_x emissions by the addition of additive. McCormick et al. [99] reported that, roughly NO_x neutral B20 biodiesel fuel derived from soybean oil could be achieved by blending biodiesel with other fuels and additives. The addition of 1% of 4-nonyl phenoxy acetic acid additive leads to improve the BTE as well as reduced the exhaust emissions [100]. The study result has been shown in Fig. 5.

Ramadhas et al. [101] investigated the performance and emission of a diesel engine using rubber seed oil with diethyl fuel additive. They found that the addition of the small percentage of diethyl ether can be used as an additive with biodiesel to improve the overall engine performance and emission characteristics. Biodiesels are formulated by blending different percentage of FAME with petroleum diesel. The use of *tert*-amyl ethyl ether (TAE) up to 5% by volume as additive significantly increases the diesel fuel properties which will also improve the biodiesel properties. Hence, better overall engine performance can be achieved [102]. Usually, catalysts do not affect the engine performance significantly but delay the ignition time and reduce the unburned hydrocarbon and the particulate matter. However, overall performance can be enhanced by adding additives with the fuel [103]. To investigate the effect of ferric chloride (FeCl_3) as an additive, a study was carried out in a direct-injection diesel engine fueled by palm oil based waste cooking oil at different operating conditions, the result revealed that BSFC reduced by 8.6% which results in an increase of BTE by 6.3%. Furthermore, significant improvement regarding emission characteristics was also observed [104]. The use of 5% by volume of diethyl ether and ethanol as an additive showed better stability in case of performance, emission and combustion of biodiesel fuel [105]. Çaynak et al. [106] studied the effect of Mn additive on viscosity of pomee biodiesel and engine performance. The results showed that the reduction in viscosity due to addition, but this had no effect on brake power.

9. Conclusion

Biodiesel has higher viscosity, higher cetane number and lower compressibility as compared to the diesel fuel. These fuel properties have an impact on engine performance, combustion and emission characteristics. The key findings of this article are as follows:

- Biodiesel has the shorter ignition delay which is prolonged with increasing biodiesel content in the blends.
- The primary reason of shorter ignition delay of biodiesel is its lower compressibility, higher viscosity and cetane number.
- The net HRR and peak cylinder pressure (PCP) of biodiesel fuel is lower than petroleum diesel due to lower heating value of the biodiesel.
- Biodiesel fuel reduces the exhaust emission such as CO, HC, and PM but increases the NO_x emission due to shorter ignition delay and advanced injection as compared to petroleum diesel.

- Both the engine performance and emissions can be ameliorated by the addition of selective antioxidants/additives.

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